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Efficient asymmetric hydrogenation with rhodium complexes of C_1-symmetric 2,5-dimethylphospholane-diphenylphosphines

Sandeep Basra,[a] Johannes G. de Vries,[b] David J. Hyett,[b] Gayle Harrison,[a] Katie M. Heslop,[a] A. Guy Orpen,[a] Paul G. Pringle*[a] and Karl von der Luehe[a]

[a] *School of Chemistry, University of Bristol, Cantocks Close, Bristol UK BS8 1TS*

[b] *DSM Pharma Chemicals-Advanced Synthesis, Catalysis & Development, P.O. Box 18, 6160 MD, Geleen, Netherlands*

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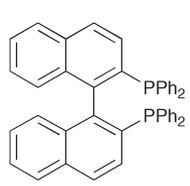
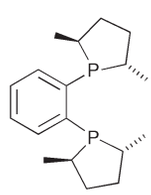
The unsymmetrical, optically active ligands 1,2-$C_6H_4(PPh_2)$((*R*,*R*)-2,5-dimethylphospholanyl) (**1a**) and the new 1,1′-$Fe(C_5H_4)_2(PPh_2)$((*R*,*R*)-2,5-dimethylphospholanyl) (**1b**) form complexes of the type $[PtCl_2(diphos)]$ (**2a,b**) and $[Rh(diphos)(diene)][BF_4]$ (**3a,b**). The crystal structure of **2a** reveals that only one quadrant is blocked. Asymmetric hydrogenation of acrylic esters and enamides using **3a** and **3b** as catalysts show that the phenylene-backboned diphosphine gives a more efficient catalyst in terms of asymmetric induction than the more flexible ferrocene-backboned diphosphine. The best results, which were obtained with **3a** and enamide substrates, exceeded those obtained with Duphos catalysts. The rate of hydrogenation of the enamides with **3a** was 10 times faster than with $[Rh(Duphos)(diene)][BF_4]$. A quadrant diagram can be used to predict the configuration of the major product, provided it is assumed to be derived from the less sterically congested intermediate.

Introduction

Asymmetric hydrogenations of C=C, C=O and C=N functionalities have found important applications in organic synthesis and in the fine chemicals business.[1] Over the last 30 years, hundreds of chiral diphosphine ligands have been screened[2] for asymmetric hydrogenation and from this empirical endeavour, some guiding principles for the design of diphosphines for efficient asymmetric hydrogenation have emerged. These include, the presence of a rigid backbone, PPh_2 groups or 2,5-dimethylphospholanes; two of the most successful chiral diphosphines, binap[3] and Duphos[4] embody these features. In parallel with the ligand work, detailed mechanistic studies[5] have illuminated the elementary steps in asymmetric hydrogenation and given rise to a useful model, based on quadrant diagrams,[6] which has been used to rationalise the efficiency of ligands such as binap and Duphos.[5]

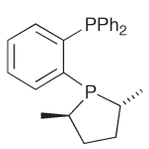


binap

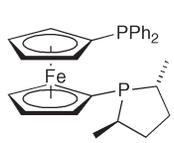


Duphos

The ligands **1a** and **1b** were designed to investigate the efficiency of a chiral diphosphine containing PPh_2 *and* 2,5-dimethylphospholane groups. Here we report the coordination chemistry of **1a** and **1b** with platinum(II) and rhodium(I) and the applications of **1a** and **1b** in asymmetric hydrogenation. While this work was in progress,[7] the synthesis of ligand[8] **1a** and some of its applications in asymmetric hydrogenation have been reported.[9]



1a



1b

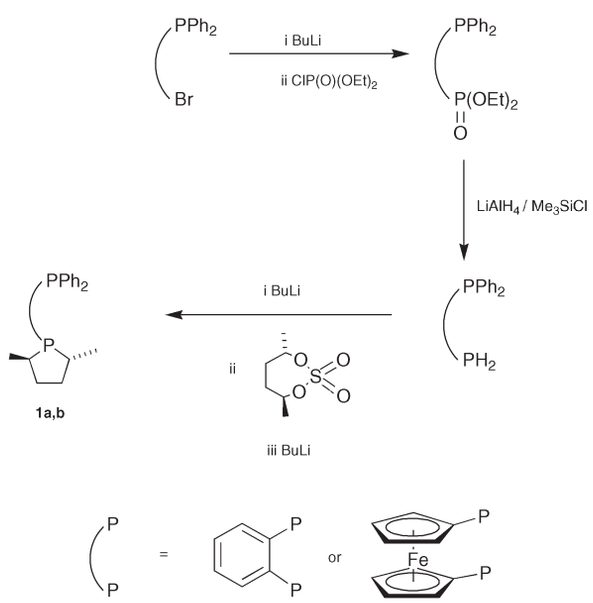
Results and discussion

Ligands **1a,b** were made according to the route shown in Scheme 1 (which is similar to the literature route[9]) and have been fully characterised. The intermediates in the synthesis of the phenylene diphosphine **1a** have been previously reported by us[10] and others,[11] while the ferrocenyl diphosphine **1b** is new and all intermediates have been fully characterised (see Experimental section).

Table 1 ^{31}P NMR data[a]

	$\delta(P_A)$	$\delta(P_B)$	$^1J(P_AP_B)$	$^1J(MP_A)$, $^1J(MP_B)$/Hz
1a	−12.1	−0.1	159	
1b	−16.7	−1.1	0	
2a	42.0	66.4	3	3468, 3666
2b	10.3	36.8	12	3807, 3664
3a	60.0	75.7	27	158, 160
3b	25.5	47.3	28	162, 158

[a] All spectra measured in $CDCl_3$ at +23 °C at 121 MHz with chemical shifts δ to high frequency of 85% H_3PO_4.



Scheme 1 Ligand synthesis.

The coordination chemistry of **1a,b** is summarised in Scheme 2 and the characterising data for the platinum(II) complexes (**2a,b**) and rhodium(I) complexes (**3a,b**) are given in Table 1 (^{31}P NMR)

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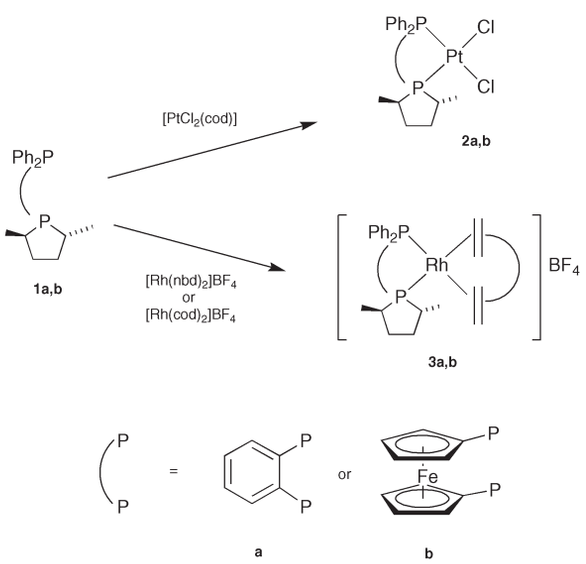
Table 2 Selected bond distances (Å) and angles (°) for **2a**

Pt(11)–P(11)	2.214(7)	P(11)–Pt(11)–P(12)	88.4(3)
Pt(11)–P(12)	2.228(8)	Cl(11)–Pt(11)–P(11)	91.4(3)
Pt(11)–Cl(11)	2.370(8)	Cl(11)–Pt(11)–P(12)	177.7(4)
Pt(11)–Cl(12)	2.343(8)	Cl(12)–Pt(11)–P(11)	177.6(3)
Pt(21)–P(21)	2.184(8)	Cl(12)–Pt(11)–P(12)	89.9(3)
Pt(21)–P(22)	2.191(6)	Cl(12)–Pt(11)–Cl(11)	90.4(3)
Pt(21)–Cl(21)	2.362(7)	P(21)–Pt(21)–P(22)	87.4(2)
Pt(21)–Cl(22)	2.374(7)	Cl(21)–Pt(21)–P(21)	90.6(2)
		Cl(21)–Pt(21)–P(22)	177.9(3)
		Cl(22)–Pt(21)–P(21)	176.9(3)
		Cl(22)–Pt(21)–P(22)	89.9(3)

Table 3 Hydrogenations of substrates **A–C**

Entry	Catalyst	Substrate	Ee
1	**3a**	**A**	81 (*R*)
2	**3b**	**A**	51 (*R*)
3	**3a**	**B**	46 (*R*)
4	**3b**	**B**	43 (*R*)
5	**3a**	**C**	82 (*S*)
6	**3b**	**C**	55 (*S*)

and in the Experimental section. The crystal structure of (*R*,*R*)-**2a** was determined (see Fig. 1 and Table 2 which lists important bond lengths and angles) and shows square-planar platinum with near equal Pt–P distances. The methyl group at C(223) blocks the upper left quadrant adjacent to the site occupied by Cl(22). Indeed the shortest methyl hydrogen to Cl(22) contact (2.85 Å) is shorter than the methine H(220)···Cl(22) contact (3.05 Å).



Scheme 2

Asymmetric hydrogenations

The rhodium complexes **3a,b** were screened for asymmetric hydrogenation of the dehydroamino acid derivatives **A** and **B** and itaconic acid **C** and the results are collected in Table 3. The catalysts were efficient in terms of conversions under mild conditions (see Experimental section for details). For all three substrates, the enantioselectivities were greater for the phenylene diphos complex **3a** than for the ferrocene diphos complex **3b**. The absolute configuration of the product from **A** was the same as that obtained with the parent Duphos catalyst but the ee's with **3a,b** were significantly inferior to the 98% ee obtained with Duphos under similar conditions.[4]

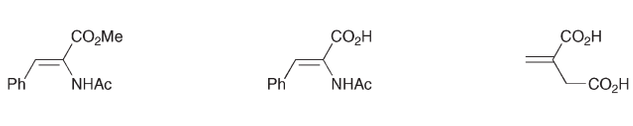


Table 4 Hydrogenations of substrates **D–H**

Entry	Substrate	Solvent	Ee
1	**D**	MeOH	12 (*S*)
2	**D**	CH_2Cl_2	38 (*S*)
3	**D**	i-PrOH	33 (*S*)
4	**E**	MeOH	42 (*R*)
5	**E**	CH_2Cl_2	42 (*R*)
6	**E**	i-PrOH	39 (*R*)
7	**F**	MeOH	94 (*R*)
8	**F**	i-PrOH	86 (*R*)
9	**G**	MeOH	95 (*R*)
10	**G**	CH_2Cl_2	70 (*R*)
11	**G**	i-PrOH	86 (*R*)
12	**G**	EtOAc	78 (*R*)
13	**H**	MeOH	96 (*R*)

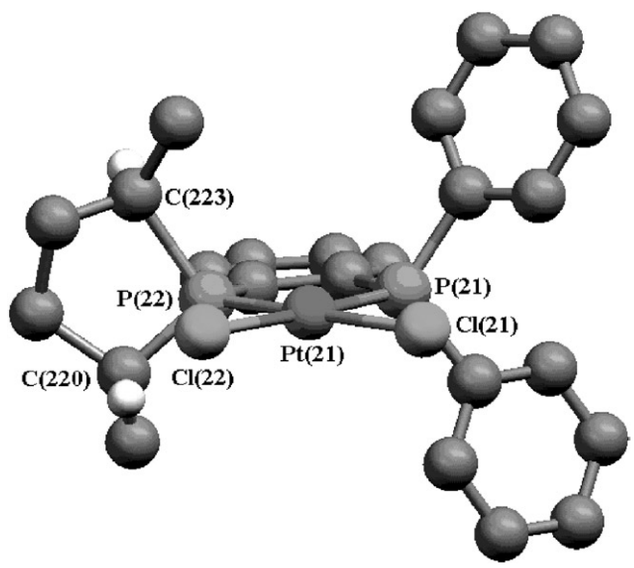
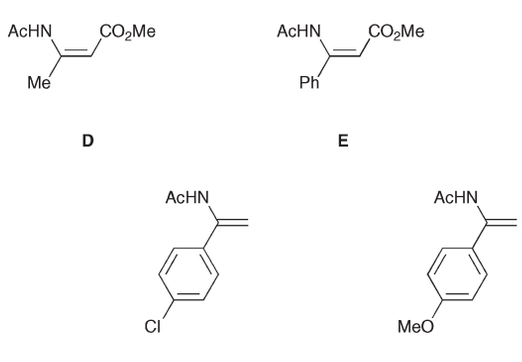


Fig. 1 Molecular structure of (*R*,*R*)-**2a**. Hydrogen atoms (other than those on tertiary carbon atoms) have been omitted for clarity.

There is commercial potential for the products of the asymmetric hydrogenation of β-amino esters **D** and **E** or enamides **F–H**.[12] The results for the hydrogenation of **D–H** with **3a** as catalyst are collected in Table 4. The enantioselectivities for **D** and **E** are disappointingly low, especially when compared to the ee's we obtained with Duphos under similar conditions in MeOH (79 and 69% for **D** and **E**, respectively). The best results obtained with **3a** were for the hydrogenation of the enamides **F–H**. The enantioselectivities were superior to the <90% ee we obtained with Duphos under similar conditions in MeOH. Saito *et al*.[9] also obtained excellent results with enamides. Our results suggest that the enantioselectivities are sometimes sensitive to the solvent used; *e.g.* see entries 9 and 10 where the ee drops from 95% in MeOH to 70% in CH_2Cl_2.



With the enamide substrates **F–H**, it was noted that the hydrogenations with **3a** as catalyst were completed much more rapidly than with [Rh(nbd)(Duphos)][BF_4] and therefore, we monitored the reaction progress more closely. Fig. 2 shows plots of the uptake of H_2 with time for substrate **F**; the rate with **3a** was over 10 times faster than with [Rh(nbd)(Duphos)][BF_4]. The source of the higher activity of **3a** is presumably the presence of the PPh_2 group. For comparison, the complex [Rh(cod){*o*-$C_6H_4(PPh_2)_2$}][BF_4] was screened and shown to be more than five times slower than **3a**. Thus it appears that the unsymmetrical catalyst **3a** is significantly more efficient than either of its symmetrical analogues.

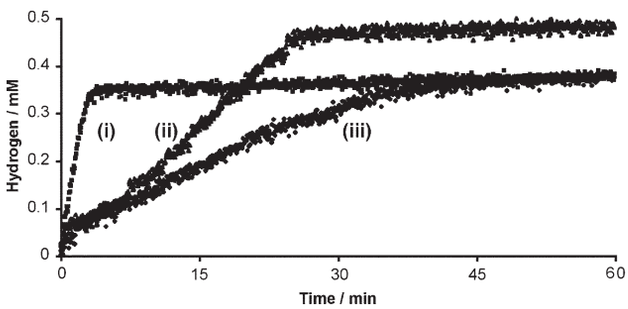


Fig. 2 Uptake of H_2 as a function of time for the hydrogenation of **F** catalysed by (i) [Rh(cod)(**1a**)][BF_4]; (ii) [Rh(cod){*o*-$C_6H_4(PPh_2)_2$}][BF_4]; (iii) [Rh(nbd)(Duphos)][BF_4].

Quadrant diagrams for Duphos catalysts have been the subject of debate recently.[5,13] They can be used to predict the absolute configuration of the hydrogenated product provided the substrate is presumed to bind to the metal in such a way that steric congestion is minimised (*i.e.* contrary to Burke's original proposal[4]). The crystal structure of (*R*,*R*)-**2a** discussed above is consistent with the quadrant diagram proposed by Saito and co-workers.[9] and shown in Fig. 3.

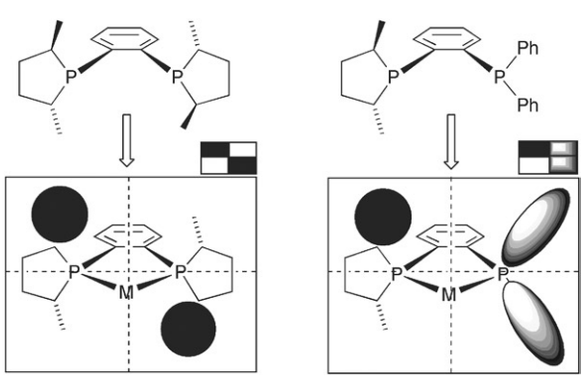


Fig. 3 Quadrant diagrams for complexes of Duphos and **1a**.[9]

From this, the configurations of the products from **A–H** can be rationalised if **A–H** bind to the metal *via* the *re*-face of the alkene. While this model is predictive, it is at odds with the observation that a Halpern-type mechanism (*i.e.* that product formation occurs from the less stable diastereoisomer of the substrate adduct) is known to operate for Duphos catalysts.[14]

Experimental

Unless otherwise stated, all reactions were carried out under a nitrogen atmosphere using standard Schlenk-line techniques. Dried, nitrogen-saturated solvents were collected from a Grubbs system[15] or obtained by refluxing under a nitrogen atmosphere over appropriate drying agents: calcium hydride (for CH_2Cl_2), sodium/benzophenone (for diethyl ether and THF). After purification, all phosphines were stored under nitrogen at room temperature. The complexes were stable to air in the solid state and were stored in air at room temperature. The starting materials prepared by literature methods were: [$PtCl_2$(cod)],[16] [$Rh(nbd)_2$][BF_4],[17] [$Rh(cod)_2$][BF_4],[18] and the *N*-acetyl-α-arylenamide substrates.[19] 1-Bromo-2-diphenylphosphinobenzene was prepared using the palladium-catalysed cross-coupling reaction reported by Stille *et al*.[20] $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and ^1H NMR spectra were recorded on a JEOL Δ300 or JEOL GX400 spectrometers; coupling constant values are given in Hz. The microanalytical laboratory of the School of Chemistry, University of Bristol, carried out elemental analyses. The mass spectrometry service, University of Bristol, recorded electron impact and fast atom bombardment mass spectra on a MD800 and an Autospec.

Preparation of 1-diphenylphosphino-2-phosphinobenzene

Chlorotrimethylsilane (1.9 cm^3, 15 mmol) was added slowly *via* syringe to a suspension of $LiAlH_4$ (0.58 g, 15 mmol) in THF (15 cm^3) at −78 °C. The mixture was stirred for 20 min, allowed to warm to room temperature and then stirred for a further 2 h. After cooling the mixture to −30 °C, a solution of 1-diethylphosphonato-2-diphenylphosphinobenzene (2.0 g, 5.0 mmol) in THF (15 cm^3) was added dropwise over 30 min and the resulting mixture was stirred at room temperature for 18 h, by which time $^{31}P\{^1H\}$ NMR spectroscopy indicated the reaction had gone to completion. The mixture was cooled with an ice–water bath and then water (7.4 cm^3) and 1 M aqueous NaOH (7.4 cm^3) added. Diethyl ether (20 cm^3) was added, the organic layer separated and the aqueous layer washed with diethyl ether (2 × 10 cm^3). The combined organic component was dried over $MgSO_4$ and then the solvent was removed under reduced pressure to give the product as a cream solid (1.43 g, 97%). Elemental analysis (%): found (calc.): C 73.4 (73.5), H 5.7 (5.5). EI mass spectrum: *m*/*z* 294 (M^+). ^{31}P ($CDCl_3$): δ −11.3 (d), −124.7 (td), ^1J(PH) 206, ^3J(PP) 98. $^{13}C\{^1H\}$ ($CDCl_3$): three groups of complex multiplets at δ 136.9–135.7, 134.0–133.2, 128.8–128.4. ^1H ($CDCl_3$): δ 3.89 (dd, 2H, PH_2, ^1J(PH) 205.9, ^4J(HH) 12.0); 6.81–6.83 (m, 2H), 7.11–7.29 (m, 10H), 7.48–7.50 (m, 2H).

Preparation of 1-diphenylphosphino-1′-phosphinoferrocene

Chlorotrimethylsilane (1.8 cm^3, 14.2 mmol) was added slowly *via* syringe to a suspension of $LiAlH_4$ (0.54 g, 14.2 mmol) in THF (15 cm^3) at −78 °C. The mixture was stirred for 20 min, allowed to warm to room temperature and then stirred for a further 2 h. After cooling the mixture to −30 °C, a solution of 1-diethylphosphonato-1′-diphenylphosphinoferrocene (2.4 g, 4.7 mmol) in THF (15 cm^3) was added dropwise over 30 min and the resulting mixture was stirred at room temperature for 18 h, by which time $^{31}P\{^1H\}$ NMR spectroscopy indicated the reaction had gone to completion. The mixture was cooled with an ice–water bath and then water (7.4 cm^3) and 1 M aqueous NaOH (7.4 cm^3) added. Diethyl ether (20 cm^3) was added, the organic layer separated and the aqueous layer washed with diethyl ether (2 × 10 cm^3). The combined organic component was dried over $MgSO_4$, concentrated to *ca.* 5 cm^3 under reduced pressure and then methanol (8 cm^3) was added. The mixture was cooled in a freezer overnight to give the product as a yellow–orange solid (1.24 g, 86%). Elemental analysis (%): found (calc.): C 64.8 (65.6), H 5.0 (5.0). EI mass spectrum: *m*/*z* 402 (M^+). ^{31}P ($CDCl_3$): δ −17.1 (s), −144.6 (t), ^1J(PH) 204. $^{13}C\{^1H\}$ ($CDCl_3$): three groups of complex multiplets at δ 133.3–133.8, 128.6–128.1, 76.6–68.6 (Cp). ^1H ($CDCl_3$): δ 3.56 (d, 2H, PH_2, ^1J(PH) 203.7); 3.87–4.32 (m, 8H, Cp), 7.19–7.37 (m, 10H).

Preparation of 1-[(2*R*,5*R*)-2,5-dimethylphospholano]-2-diphenylphosphinobenzene (1a)

1-Diphenylphosphino-2-phosphinobenzene (1.10 g, 3.74 mmol) was dissolved in THF (45 cm^3) and *n*-BuLi (2.3 cm^3, 3.74 mmol, 1.6 M solution in hexane) was added dropwise at room temperature. The deep red solution was stirred for 90 min, after which time a solution of (2*S*,5*S*)-2,5-hexanediol cyclic sulfate (0.67 g, 3.74 mmol) in THF (6 cm^3) was added dropwise giving an orange solution. The mixture was then stirred for 2 h, and then another portion of *n*-BuLi (2.55 cm^3, 5.05 mmol, 1.6 M solution in hexane) was added dropwise, again giving a deep red solution. After stirring for a further 2 h, any excess *n*-BuLi was quenched with methanol (2 cm^3) and the yellow–orange mixture was filtered through Celite to remove the gelatinous precipitate. The yellow filtrate was concentrated to 5 cm^3 and pentane (25 cm^3) was added. The white precipitate was filtered off and the solvent removed to give the product as a viscous white oil

(0.9 g, 64%). EI mass spectrum: *m*/*z* 376 (M^+). ^{31}P ($CDCl_3$): δ −12.1 (d), −0.1 (d), ^3J(PP) 159.2. The optical purity of **1a** was determined to be >99.5% by a ^{31}P NMR method: reaction with the *R*-enantiomer of the orthometallated complex[21] $[Pd_2Cl_2(Me_2NCHMeC_6H_4)_2]$ gave a product for which a single pair of two doublets at δ 72.0 and 41.7, ^2J(PP) 22, were observed; a different set of doublets (δ 73.5 and 41.0, ^2J(PP) 22) were observed for the diastereoisomeric product formed when the *S*-enantiomer was used.

Preparation of 1-[(2*R*,5*R*)-2,5-dimethylphospholano]-1′-diphenylphosphinoferrocene (1b)

To a solution of 1-diphenylphosphino-1′-phosphinoferrocene (0.50 g, 1.24 mmol) in THF (20 cm^3) was added *n*-BuLi (0.78 cm^3, 1.24 mmol, 1.6 M in hexane) dropwise *via* syringe and the orange solution became deep red. After stirring for 90 min, a solution of (2*S*,5*S*)-2,5-hexanediol cyclic sulfate (0.22 g, 1.24 mmol) in THF (4 cm^3) was added dropwise and the mixture was stirred for 2 h. A second portion of *n*-BuLi (0.85 cm^3, 1.37 mmol, 1.6 M solution in hexane) was then added, and again the solution became deep red. After stirring for a further 2 h, the mixture was quenched with methanol (2 cm^3), and filtered through Celite. The filtrate was concentrated to 5 cm^3, pentane (20 cm^3) added and the mixture was placed in the freezer overnight. The precipitate was removed by filtration and the solvent removed *in vacuo* to give the product as an orange oil (0.4 g, 67%). EI mass spectrum: *m*/*z* 484 (M^+). ^{31}P ($CDCl_3$): δ −16.7 (s), −1.1 (s). ^1H ($CDCl_3$): δ 0.60 (dd, 3H, CH_3), 0.80 (m, 1H, CH), 1.18 (m, 1H, CH), 1.25 (dd, 3H, CH_3), 1.70–1.86 (m, 2H, CH_2), 2.01–2.14 (m, 1H, CH_2), 2.28–2.41 (m, 1H, CH_2), 3.75 (s, 1H, Cp), 3.97 (s, 1H, Cp), 4.01 (m, 1H, Cp), 4.07–4.13 (m, 3H, Cp), 4.27 (s, 1H, Cp), 4.33 (s, 1H, Cp), 7.19–7.32 (m, 10H, Ph).

Preparation of $[PtCl_2(1a)]$ (2a)

A solution of **1a** (90 mg, 0.24 mmol) and $[PtCl_2(cod)]$ (90 mg, 0.24 mmol) in dichloromethane (5 cm^3) was stirred overnight. Diethyl ether (10 cm^3) was added to the yellow solution and the precipitate collected to give the product as a cream solid (120 mg, 78%). FAB mass spectrum: *m*/*z* 607 [(M^+) − Cl]. Elemental analysis (%): found (calc): C 41.5 (41.3), H 4.1 (3.9). ^{31}P ($CDCl_3$): δ 66.4 (d, ^1J(PtP) 3666), 42.0 (d, PPh_2, ^1J(PtP) 3468), ^2J(PP) 3). $^{13}C\{^1H\}$ ($CDCl_3$): δ 134.1–131.8 (m, Ph), 129.0–131.8 (m, Ph), 40.9 (d, CH, ^1J(CP) 38.4), 36.8 (d, CH, ^1J(CP) 37.9), 35.8 (d, CH_2, ^2J(CP) 4.6), 31.0 (s, CH_3), 17.0 (d, CH_2, ^2J(CP) 4.4), 13.9 (s, CH_3). ^1H ($CDCl_3$): δ 0.95 (dd, 3H, CH_3, ^3J(HH) 7.1, ^3J(PH) 19.4), 1.48 (dd, 3H, CH_3, ^3J(HH) 6.8), ^3J(PH) 19.4), 1.67–1.80 (m, 1H, CH_2), 2.18–2.79 (m, 4H, CH_2/CH), 3.59–3.63 (m, 1H, CH), 7.42–7.80 (m, 14H, Ph).

Preparation of $[PtCl_2(1b)]$ (2b)

A solution of **1b** (95 mg, 0.2 mmol) and $[PtCl_2(cod)]$ (73 mg, 0.2 mmol) in dichloromethane (10 cm^3) was stirred overnight. The solution was then concentrated to *ca*. 2 cm^3 and diethyl ether (6 cm^3) was added. The precipitate was collected to give the product as an orange solid (120 mg, 82%). Elemental analysis (%): found (calc): C 45.1 (44.8), H 4.0 (4.1). ^{31}P ($CDCl_3$): δ 36.8 (d, ^1J(PtP) 3664), 10.3 (d, ^1J(PtP) 3807), ^2J(PP) 12. $^{13}C\{^1H\}$ ($CDCl_3$): δ 136.4–127.6 (m, Ph), 75.8–70.2 (m, Cp), 35.0 (d, CH, ^1J(CP) 38.9), 33.8 (d, CH, ^1J(CP) 39.1), 33.4 (s, CH_2), 22.1 (s, CH_2), 15.3 (s, CH_3), 13.9 (s, CH_3). ^1H ($CDCl_3$): δ 0.98 (dd, 3H, CH_3, ^3J(HH) 7, ^3J(PH) 17.1), 1.37 (dd, 3H, CH_3, ^3J(PH) 20.1), 1.45 (m, 2H, CH_2), 1.88–1.97 (m, 2H, CH_2), 2.29 (m, 1H, CH), 2.70 (m, 1H, CH), 3.90 (s, 1H, Cp), 4.28–4.38 (m, 4H, Cp), 4.53 (s, 1H, Cp), 4.63 (s, 1H, Cp), 4.90 (s, 1H, Cp), 7.15–7.2 (m, 1H, Ph), 7.39–7.47 (m, 4H, Ph), 7.6–7.64 (m, 1H, Ph), 7.78–7.84 (m, 2H, Ph), 8.03–8.1 (m, 2H, Ph).

Preparation of [Rh(norbornadiene)(1a)][BF_4] (3a)

To a solution of **1a** (220 mg, 0.58 mmol) in CH_2Cl_2 (8 cm^3) was added $[Rh(nbd)_2][BF_4]$ (219 mg, 0.58 mmol) and the red solution was allowed to stir overnight. Addition of diethyl ether (15 cm^3) resulted in the formation of a precipitate and after stirring for 1 h, the solid was collected to afford the product as an orange–brown solid (385 mg, 75%). FAB mass spectrum: *m*/*z* 571 [(M^+) − BF_4]. Elemental analysis (%): found (calc): C 53.9 (54.0), H 5.0 (5.0). ^{31}P ($CDCl_3$): δ 75.7 (dd, ^1J(RhP) 160), 60.0 (dd, ^1J(RhP) 158), ^2J(PP) 27. ^1H ($CDCl_3$): δ 1.0 (dd, 3H, CH_3, ^3J(HH) 7.2, ^3J(PH) 15.4), 1.4 (dd, 3H, CH_3, ^3J(HH) 7, ^3J(PH) 19.1), 1.51 (m, 1H, CH), 1.83 (d, 1H, nbd), 1.96 (d, 1H, nbd), 2.36 (m, 1H, CH), 2.38–2.46 (m, 2H, CH_2), 2.69–2.78 (m, 2H, CH_2), 4.25 (s, 1H, nbd), 4.29 (s, 1H, nbd), 5.07 (s, 1H, nbd), 5.33 (s, 1H, nbd), 5.96 (m, 2H, nbd), 7.35–7.78 (m, 14H, Ph). The complex [Rh(cod)(**1a**)][BF_4] was made similarly from $[Rh(cod)_2][BF_4]$.

Preparation of [Rh(nbd)(1b)][BF_4] (3b)

To a solution of **1b** (630 mg, 1.3 mmol) in dichloromethane (50 cm^3) was added $[Rh(nbd)_2][BF_4]$ (486 mg, 1.3 mmol) and the solution was stirred overnight. The solution was concentrated to 10 cm^3, diethyl ether (30 cm^3) and pentane (10 cm^3) were added and, after stirring for 1 h, the precipitate was collected to afford the product as an orange–brown solid (735 mg, 74%). FAB mass spectrum: *m*/*z* 679 [(M^+) − BF_4]. Elemental analysis (%): found (calc): C 52.7 (52.7), H 5.2 (4.9). ^{31}P ($CDCl_3$): δ 47.3 (dd, ^1J(RhP) 158), 25.5 (dd, ^1J(RhP) 162), ^2J(PP) 28. ^1H ($CDCl_3$): δ 0.89 (dd, 3H, CH_3, ^3J(HH) 7.3, ^3J(PH) 14.8), 1.26 (m, 1H, CH), 1.38 (d, 1H, nbd), 1.6 (d, 1H, nbd), 1.81 (m, 2H, CH_2), 1.88 (dd, 3H, CH_3, ^3J(HH) 7.1, ^3J(PH) 19.6), 1.93 (m, 1H, CH), 2.30 (m, 1H, CH_2), 2.96 (m, 1H, CH_2), 11 broad singlets at δ 3.72, 3.92, 4.03, 4.21, 4.32, 4.39, 4.45, 4.63, 4.69, 4.77, 4.98 (14H, Cp, nbd), 7.29–7.34 (m, 2H, Ph), 7.43 (s, 3H, Ph), 8.05–8.08 (m, 2H, Ph).

Standard experimental procedure for asymmetric hydrogenation of substrates A–C

A 50 cm^3 glass vessel was placed in the steel autoclave and the reactor was sealed. The reactor was deoxygenated three times with nitrogen, evacuated and then sealed under vacuum and the temperature of the reactor was set to the required value. A methanolic (10 cm^3) solution containing [Rh(nbd)(**1a**)][BF_4] or [Rh(nbd)(**1b**)][BF_4] (0.02 mmol), the substrate (2 mmol) and triethylamine (0.28 ml, 2 mmol) was syringed into the glass vessel. A pressure of 1 bar hydrogen was applied, the reactor sealed and the solution stirred for 20 h. The pressure was then released, the reactor opened and the reaction mixture worked-up as follows. The solvent was removed from the solution taken from the autoclave by rotary evaporation and the residue was cooled in an ice-bath and dissolved in NaOH (5 cm^3, 0.5 M solution). The insoluble material was filtered off and the filtrate was acidified with 2 M HCl. The solution was extracted with diethyl ether (3 × 5 cm^3) and the combined organic fractions dried over $MgSO_4$. The solvent was removed by rotary evaporation to give the product as a white solid. For substrate **A**, the ee of the product was determined by chiral GC (L-Chiracel-Val from Chrompack, 300 °C). For substrates **B** and **C** the ee of the products were calculated from polarimetry by comparison of the specific rotation of the product with literature values of an authentic sample (for *N*-acetyl-(*R*)-phenylalanine **B**, $[\alpha]_D^{26} = -51.8$ (*c* = 1, solvent = EtOH); for (*R*)-(−)-methyl succinic acid **C**, $[\alpha]_D^{20} = +16.88$ (*c* = 2.16, solvent = EtOH)).

Standard experimental procedure for asymmetric hydrogenation of substrates D–H

Catalyst [Rh(cod)(**1a**)][BF_4] (0.010 mmol) and the substrates (1.0 mmol) were mixed in glass vessels. Up to eight vessels were placed in the Endeavor™ parallel screening apparatus and flushed with nitrogen. The nitrogen-saturated solvent was added (5.0 cm^3) and the apparatus sealed. The vessels were purged 10 times with nitrogen and once with hydrogen. The autoclave was pressurised with 5 bar H_2 and the reaction mixture stirred for 3 h. The resulting mixture was filtered through a 1.5 cm pad of silica to remove the metal complex catalyst. The conversion was measured by ^1H NMR spectroscopy and ee determination by chiral HPLC (for **H**) using a Chiralpak AD 250 × 4.6 mm column; *n*-hexane–i-PrOH (92 : 8, v/v) or chiral GC (for **D–G**) using a CP Chiracel-Dex CB column from Chrompack (25 m × 0.25 mm × 0.25 μm), operated at 150 °C or 160 °C. Racemates were used to check the technique. Absolute configurations

were determined by comparison with reference compounds and literature values.[22] Retention times for the products from substrate **D** were 11.08 and 11.27 min, from substrate **E** were 37.50 and 38.10 min, from substrate **F** were 5.1 and 5.5 min, from substrate **G** were 6.3 and 6.6 min and from substrate **H** were 22 and 27 min.

X-Ray crystal structure of (*R*,*R*)-2a. X-Ray diffraction experiments on (*R*,*R*)-2a as its dichloromethane solvate were carried out at −100 °C on a Bruker SMART diffractometer using Mo-Kα X-radiation, $\lambda = 0.71073$ Å. Crystal and refinement data for (*R*,*R*)-[$PtCl_2$\{(MeC_4H_6Me)$PC_6H_4PPh_2$\}]·CH_2Cl_2, **2a**·CH_2Cl_2: $C_{25}H_{28}Cl_4P_2Pt$, $M = 727.3$, triclinic, space group $P\bar{1}$ (no. 1), $a = 10.057(3)$, $b = 10.276(3)$, $c = 14.575(4)$ Å, $\alpha = 92.175(5)$, $\beta = 102.839(5)$, $\gamma = 114.204(4)°$, $V = 1325.4(6)$ Å^3, $Z = 2$, $\mu = 5.83$ mm^{-1}, $T = 173(2)$ K, 8686 unique data, $R_{int} = 0.034$, R_1 (for all 7884 data with $F^2 > 2\sigma(F^2)$) = 0.059. Absorption corrections were based on equivalent reflections and structures refined against all F_o^2 data with hydrogen atoms riding in calculated positions. The analysis is hampered by the presence of a local near-centre of symmetry between the two independent molecules in the $P\bar{1}$ unit cell. The $PtCl_2PC_6H_4PPh_2$ units of the two molecules are essentially exactly related by this pseudo-inversion centre. The resultant refinement is consequently rather unstable and has large difference electron features close to the platinum atoms presumably resulting from poor absorption correction that is not in this case concealed by, *e.g.* the anisotropic displacement parameters of those atoms. Alternative refinement models with *S*,*S*-configuration of the phospholane or $P\bar{1}$ symmetry gave significantly worse residuals.

CCDC reference number 235219.

See http://www.rsc.org/suppdata/dt/b4/b404827j/ for crystallographic data in CIF or other electronic format.

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